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Monte Carlo simulation of cluster diffusion in a triangular lattice

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Cluster diffusion on a surface has been simulated with a triangular-lattice-gas model and the kinetic Monte Carlo method. The dependence with temperature and cluster size and the detailed mechanisms of cluster motion have been studied, as well as the role of impurities. Results show that cluster motion occurs through a mechanism in which random atomic displacements along the cluster perimeter make it deform and crawl. In contrast, evaporation-condensation has a negligible role at low temperatures. If impurities with a lower binding energy are added, they concentrate at the cluster perimeter and greatly facilitate cluster motion by lowering activation energies, provided that atom-impurity exchanges are possible.

Cluster diffusion on surfaces has a clearly important role in many technologically important processes like heterogeneous catalysis and crystal growth. Diffusion of individual atoms and clusters has been studied for a long time with field ion microscopy[1] and, more recently, with scanning tunneling microscopy (STM).[2,3] Two recent STM experiments suggest that impurities may have a dramatic effect on the cluster dynamics. On the one had, clusters artificially formed on a Au(111) surface under ambient-pressure conditions[4,5] seem to be much more stable than those made by a similar technique in ultrahigh vacuum,[6] suggesting that chemisorbed or physisorbed molecules may pin down the clusters and *reduce* their mobility.[7] On the other hand, a recent STM experiment by de la Figuera *et al.*[8] shows large diffusion of clusters of vacancies on a Cu(111) surface. The diffusion coefficient decreases with cluster size and *increases* dramatically when a small concentration of cobalt atoms is deposited on the surface. These cobalt atoms are not directly visible in the STM images and they are possibly incorporated to the first or second substrate layer, forming some kind of surface alloy or sandwich.[9]

From a theoretical point of view, there have been several lattice-gas kinetic Monte Carlo[10] simulations, which have studied the dependence of the cluster's diffusion coefficient D_l with cluster size l in a square[11,12] or triangular[13] lattice. An apparent $D_l \sim l^{-1.05}$ dependence was interpreted[12] in terms of several possible mechanisms for cluster motion: (1) diffusion of individual atoms along the cluster perimeter, giving rise to a $D_l \sim l^{-3/2}$ dependence; (2) evaporation and condensation of atoms at random positions of the cluster perimeter, yielding $D_l \sim l^{-1/2}$; (3) a third mechanism, namely, diffusion of vacancies across the cluster, would itself yield $D_l \sim l^{-1}$, but it was discarded in favor of a crossover between the first two mechanisms, because of its likely lower probability.

In some of these studies,[10-12] an ensemble of clusters of varying size was observed to diffuse during a short enough time for their sizes not to change too much, at a relatively high temperature. In other studies[13] a fixed size of the cluster was enforced by not allowing atoms to evaporate. On the other hand, the role of impurities on cluster evaporation has been explored by Bitar *et al.* using a kinetic Monte Carlo lattice model with more complex interactions.[7] They conclude that, under certain conditions, impurities will severely decrease the rate at which atoms evaporate from the cluster.

In this paper I further analyze the mechanism of cluster diffusion at the relatively low temperatures relevant to diffusion experiments of seconds or longer. In fact, if we measure lengths in units of the lattice constant and time in units of the "trial time" for individual atom jumps, then we would ideally be interested in diffusion rates of the order of 10^{-12}. The second aim of this paper is to make a first approach to the influence of impurities on cluster diffusion.

As in previous simulations, I have used the kinetic spin-exchange Ising model,[14] but allowing also for zero spin, in addition to the usual ±1 values:

$$E = -J \sum_{\langle ij \rangle} s_i s_j \ , \tag{1}$$

where $\langle ij \rangle$ means nearest-neighbor pairs and $s_i = \{-1, 0, +1\}$. Spin exchanges are allowed only between nearest-neighbor sites, one at a time, with probability

$$P_{ij} = [1 + \exp(\Delta E_{ij} / k_B T)]^{-1} \ , \tag{2}$$

where ΔE_{ij} is the energy change associated with the exchange of spins in sites i and j. It is very simple to show that this model is equivalent to a lattice-gas model with three different species A, B, and C, which I interpret, in relation to the STM experiments, as normal atoms, impurities, and vacancies, respectively,

$$E = \sum_{\langle ij \rangle} \epsilon_{s_i s_j} \ , \tag{3}$$

where $\epsilon_{AA} = -4J$, $\epsilon_{AB} = -2J$, $\epsilon_{BB} = -J$, and $\epsilon_{AC} = \epsilon_{BC} = \epsilon_{CC} = 0$.

This is equivalent to the so-called ABV model,[15,16] with interaction parameters intermediate between cases (i) and (ii) of Ref. 15, and with vacancies in that model playing the role of B atoms here. In the absence of B atoms the system is the ordinary ferromagnetic Ising model, with a critical temperature $k_B T_c/\epsilon_{AA}=0.910\,239$ ($k_B T_c/J=3.640\,957$) for the triangular lattice used.[17] Since the interaction between A and B atoms is weaker than between A atoms, the two species will tend to segregate.[18] The same is true between B atoms and vacancies, the result being that B atoms tend to concentrate in the interface between A atoms and vacancies.

For the purpose of studying cluster diffusion, I create a cluster of N_A A atoms and N_B B atoms in the center of an otherwise empty unit cell (i.e., full of C atoms) with periodic boundary conditions. For clarity I will consider a cluster of A atoms surrounded by B atoms and vacancies. However, since the model is symmetric with respect to a change of sign of all the spins, it can equally well be interpreted as a cluster of vacancies surrounded by A and B atoms as in the mentioned STM experiments.[8] For sufficiently low temperatures like those considered in this work, the cluster integrity is maintained during the whole simulation, with a very small fraction of evaporated gas atoms of type A, in equilibrium with the cluster. Therefore, despite the absence of constraints over evaporations from the cluster, its size is essentially constant and its center of mass is readily identifiable, while maintaining thermal equilibrium during arbitrarily long simulations. When an A atom evaporates or condenses, the resulting displacement of the center of mass is recorded separately, and the same is done when a vacancy moves through the cluster. Thus, the relative contribution to the diffusion coefficient of the three mechanisms described above[12] can be easily quantified.

Finite-size effects deserve a special mention. Although the calculated diffusion coefficients were not observed to depend on the cell size for a wide range of sizes, a problem occurred for the smallest cluster sizes and the highest temperatures. In this case, the cluster's vapor pressure is relatively high and the fraction of gas atoms is no longer negligible for large cells. The problem disappears with smaller cells (though still much larger than the cluster).

A different problem occurred for the lowest temperatures and largest cluster sizes. In these conditions some atoms would move back and forth along the cluster perimeter, producing a small random motion of the cluster's center of mass but without giving rise to a true diffusion. In other words, very long self-correlation times occurred in this case and extremely long simulations were required. As a safeguard, only sampling intervals for which the average cluster displacements were larger than one lattice constant were considered, and it was systematically checked that the diffusion coefficient did not depend on the sampling interval.

Figure 1 shows an Arrhenius plot of the diffusion coefficient for a cluster of 300 A atoms and no B atoms. The individual contributions of mechanisms (2) and (3) mentioned above are also shown. These are defined as the diffusion coefficients that would occur if only cluster motions due to those processes were considered. It can be seen that, for the temperature studied, these contributions are negligible and only mechanism (1) is relevant.

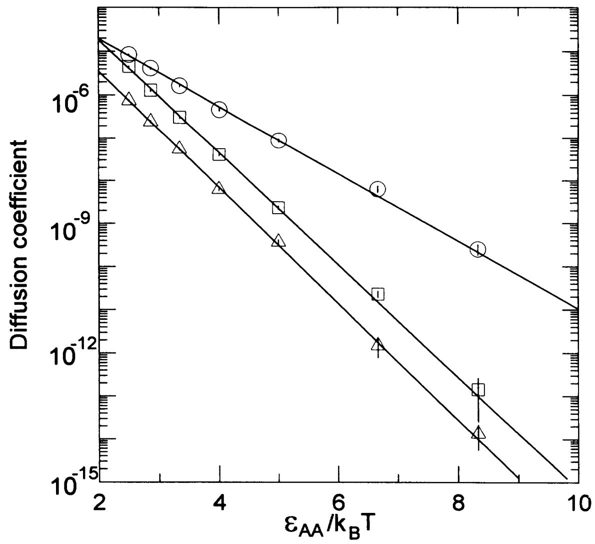

FIG. 1. Arrhenius plot of the cluster diffusion coefficient for a cluster of 300 atoms in a triangular lattice with periodic boundary conditions (circles). Also shown are the separated contributions to cluster diffusion of evaporation-condensation processes (squares) and a vacancy motion inside the cluster (triangles). The remaining (and main) contribution is that of atoms moving along the cluster perimeter.

Figure 2 shows the fitted activation energies for the total diffusion coefficient, and for the contributions of mechanisms (2) and (3), as a function of cluster size. As expected, mechanisms (2) and (3) have activation energies close to $3\epsilon_{AA}$, the sublimation energy in this model, and also the energy associated to an isolated vacancy. Also as expected, mechanism (1) has the lowest activation energy, with a value intermediate between ϵ_{AA} (the energy bar-

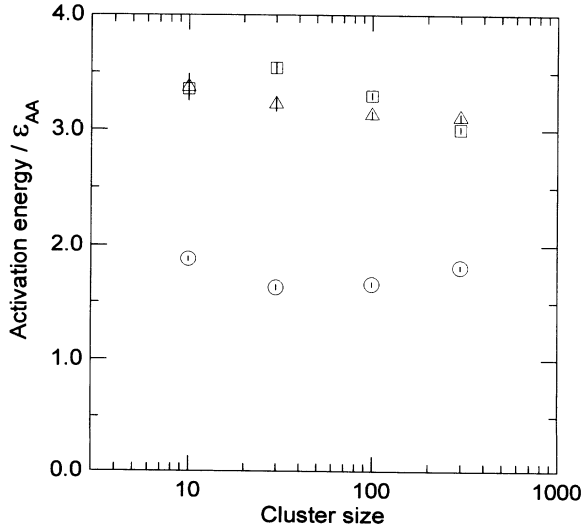

FIG. 2. Activation energies for cluster diffusion and for the separated contributions of evaporation-condensation and vacancies.

rier for moving an atom from a kink to the "down" step) and $2\epsilon_{AA}$ (the barrier for moving it to the "up" step). Despite the symmetry of the model with respect to spins $+1$ and -1 (evaporated atoms and cluster vacancies), the very different prefactor of mechanisms (2) and (3) (see Fig. 1) can be explained by the surface contribution to the cluster energy: while evaporations decrease the perimeter length, cluster vacancies increase it.

Figure 3 shows the size dependence of D_l at a fixed temperature, and the contribution of mechanisms (2) and (3). Figure 4 presents the adjusted power exponents y such that $D_l \sim l^{-y}$, as a function of temperature. It can be seen that the expected values $y = -\frac{3}{2}, -\frac{1}{2}, -1$ are not reproduced in the simulations, except for the first one. I attribute this failure to the absence of surface-energy effects in the theoretical predictions. These effects will increase evaporation rates for small clusters, relative to large ones, thus increasing the exponent y for process (2). But the opposite will occur for vacancy formation rates, decreasing the exponent y for process (3).

Figure 5 shows the dependence of D_l, for a cluster of 100 A atoms, on the concentration of B atoms in the gas phase. This concentration is defined as the average number of B atoms not linked to the cluster, divided by the average number of lattice sites not occupied by the cluster In practice, those concentrations were obtained by changing the number of B atoms between 1 and 100 in a cell of 1024 sites. It can be seen that the diffusion coefficient is enhanced by two orders of magnitude by the B impurities. However, a word of caution is necessary in order to interpret the STM experiments of de la Figuera *et al.* in terms of the above effect. In the model studied, equal exchange rates are assumed between AB, AC, and BC pairs, and those exchanges are essential to obtain the result of Fig. 5. In fact, if either AB or BC exchanges are forbidden, cluster diffusion *decreases* when B atoms are added. This result is interpreted as follows: as mentioned above, B atoms tend to concentrate on the interface between A and C phases, i.e., on the cluster surface. When atom-atom exchanges are present, B atoms decrease activation energies because the energy increase of an AB exchange is lower than that of an AC exchange. But if atom-atom exchanges are forbidden, those same B atoms, which stick to kinks at the cluster surface, now block the surface mobility and the cluster diffusion. In

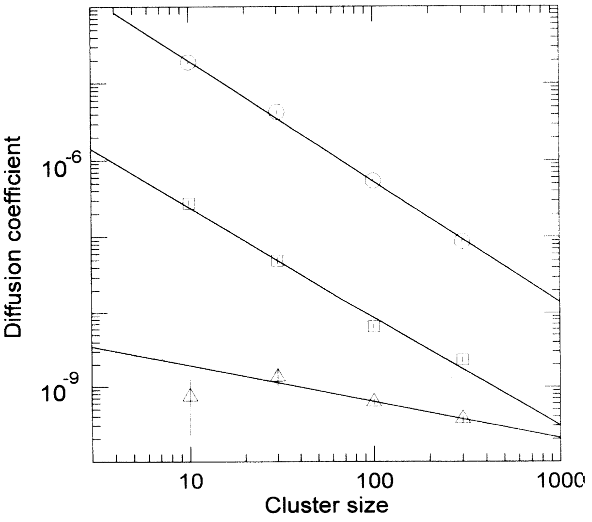

FIG. 3. Size dependence of the cluster diffusion coefficient and of the two separated contributions mentioned in Fig. 1. The temperature is $0.2\epsilon_{AA}/k_B$.

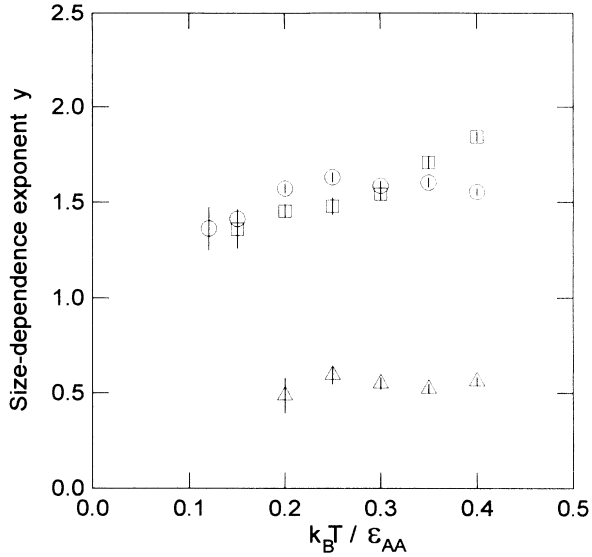

FIG. 4. Temperature dependence of the exponent y for the size dependence of the cluster-diffusion coefficient $D_l \sim l^{-y}$, and for the contributions of evaporation-condensation and vacancies.

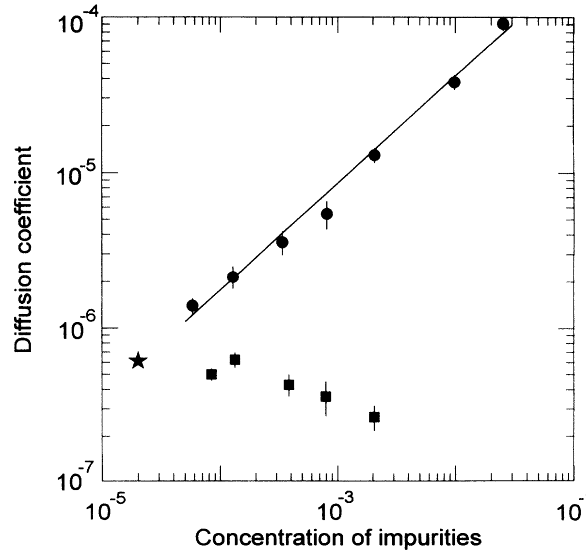

FIG. 5. Circles: dependence of the cluster-diffusion coefficient on the concentration of impurities, represented in an Ising model by spin value zero, in addition to $+1$ (atoms) and -1 (vacancies). All spin exchanges are permitted. Squares: the same but without exchanges between spins 0 and $+1$ (atoms and impurities). The ordinate of the star is the diffusion coefficient in the absence of impurities.

practice, although atom-exchange processes are well documented in surfaces,[19,20] it is unlikely that such processes may be as frequent as atom-vacancy exchanges. Therefore, depending on the specific energy barriers for each process in a given surface, cluster diffusion may either increase or decrease when impurities are added. This in turn may explain the increased stability of gold clusters formed by STM manipulation in ambient-pressure conditions,[4,5] with respect to those formed in ultrahigh vacuum[6] and, at the same time, the increased mobility in copper clusters when cobalt impurities are deposited on the surface.[8]

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